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EVALUATION OF A BROMINATED RESIN SYSTEM FOR FERRICYANIDE BLEACH--ETC(U)
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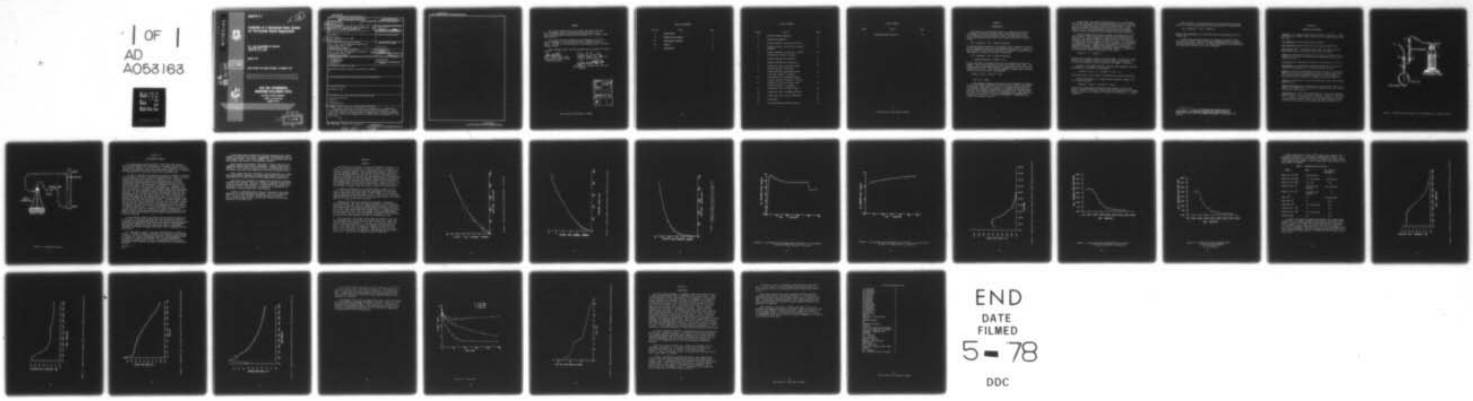

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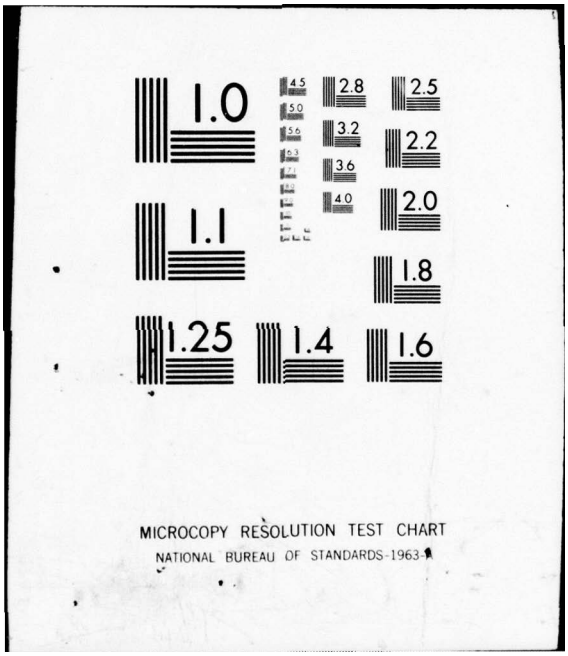
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Evaluation of a Brominated Resin System for Ferricyanide Bleach Regeneration

DET 1, CIVIL AND ENVIRONMENTAL ENGINEERING
DEVELOPMENT OFFICE, ADTC
TYNDALL AFB, FB FA 32403

MARCH 1978

CEEDO

FINAL REPORT FOR PERIOD OCTOBER 1974-MARCH 1975

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CIVIL AND ENVIRONMENTAL
ENGINEERING DEVELOPMENT OFFICE
(AIR FORCE SYSTEMS COMMAND)
TYNDALL AIR FORCE BASE
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Brominated resins were evaluated in the laboratory for regenerating ferricyanide bleaches from Air Force photoprocessing laboratories. Several resins were tested to determine bromine transfer rates. Results showed the technique is technically feasible but too complicated and hazardous for small photo labs.

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PREFACE

This report summarizes work done under job order 2103-7W-20. First Lieutenant Dale H. Allen was project engineer for Det 1, Civil and Environmental Engineering Development Office (CEEDO), ADTC, Tyndall AFB FL.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

The formation of photographic images is caused by the action of a developer on exposed silver particles. When light strikes these silver particles, a latent image is formed. The developer, acting only on these exposed silver particles, reduces the silver to metallic silver:

$$Ag^{+} + \text{developer} \rightarrow Ag^{O} + \text{oxidized developer}$$

In black and white processing, this metallic silver produces the images, and the undeveloped silver must be removed by the action of a fixer. In color processing, the image is formed by the reaction of oxidized color developers with couplers to produce colored dyes:

$$Ag^{+} + \text{developer} \rightarrow Ag^{O} + \text{oxidized developer}$$

$$\text{oxidized developer} + \text{coupler} \rightarrow \text{dye}$$

Because the image is produced by the dye, the metallic silver must be removed. This is done through the action of a bleach and a fixer. The bleach converts the metallic silver to a soluble salt so that it can be removed by the fixer. There are many chemicals suitable for the bleaching function, one of which is ferricyanide:

$$Fe(CN)_6^{-3} + Ag^{O} \rightarrow Fe(CN)_6^{-4} + Ag^{+}$$

$$Ag^{+} + Br^{-} \rightarrow AgBr$$

As ferrocyanide builds up and bromide and ferricyanide are removed, the solution becomes unsuitable for use and must be either replenished or discarded. When used in a properly run photoprocessing shop, the solutions are constantly replenished by a slightly concentrated bleach solution, with constant overflow from the bleach tank. The replenishment rate for a particular film is recommended by the manufacturer, but, in practice, this rate is changed by the operator to compensate for changes in processing results.

In many cases, the overflow from the bleach tank is discharged into the sanitary sewer where hexacyanoferrates pass almost unchanged through the treatment plant and into the receiving water. There, the action of sunlight and oxygen cause the release of free cyanide. Because of this, the Environmental Protection Agency has proposed strict limits on the amount of total cyanide that may be discharged.

Several methods are available to remove hexacyanoferrates from waste streams. Among these are precipitation with ferrous sulfate, ozonation, and chlorine oxidation. Other methods are available to regenerate the bleach to make it suitable for reuse. The requirements of regeneration are the oxidation of the ferrocyanide to ferricyanide, the replacement of the bromide, and concentration of the solution to replenisher strength. Regeneration methods include electrolysis, ozonation, persulfate oxidation, and bromine oxidation. Regeneration by electrolysis produces ferricyanide at the anode:

$$Fe(CN)_6^{-4} + e^- \rightarrow Fe(CN)_6^{-3}$$

Bromide must be added, usually as sodium bromide. Although the equipment for this scheme is costly, the results have been excellent. At one Air Force facility, over 90 percent of the bleach is recycled.

Ozonation is a complex process, involving many different reactions. Ferrocyanide is oxidized to ferricyanide:

$$2Fe(CN)_6^{-4} + H_2O + O_3 \rightarrow 2Fe(CN)_6^{-3} + 2OH^- + O_2$$

The capital cost of this process is prohibitive for small facilities.

Persulfate oxidation is a commonly used technique, capable of 60 to 70 percent recycle:

$$2Fe(CN)_6^{-4} + S_2O_8^{-2} \rightarrow 2Fe(CN)_6^{-3} + 2SO_4^{-2}$$

Unlike other regeneration techniques, where sodium is the only by-product, sulfate is produced, reducing the reuse potential of the bleach. However, because of its simplicity, persulfate regeneration is a common technique.

Bromine oxidation is theoretically the best regeneration technique, bromine is added stoichiometrically with the oxidation of ferrocyanide:

$$Br_2 + 2Fe(CN)_6^{-4} \rightarrow 2Br^- + 2Fe(CN)_6^{-3}$$

However, because bromine is a very toxic gas, this technique is not in general use.

A method of regeneration without the hazards of handling bromine has become available. This method uses an impregnated resin to release bromine to the bleach solution. An earlier investigation[1] has demonstrated the theoretical feasibility of such a technique.

---

[1] Lotz, R. E. Use of a Brominated Ion-Exchange Resin for Regeneration of Photographic Ferricyanide Bleach Solutions, AFWL-DE-TN-73-025, Air Force Weapons Laboratory, Kirtland AFB, NM, Jun 1973

SECTION II

MATERIALS AND METHODS

Glassware. All glassware was of pyrex, washed in detergent, rinsed with tap water, 6N HCl or HNO_3, tap water, and distilled water before each use.

All Chemicals were ACS reagent grade or better.

Distilled water was obtained from an all-glass Corning® still.

Spent bleach (ME^{-4}) was obtained every three days from the photo-processing facility, Kirtland Air Force Base, New Mexico.

Bromine was measured by transferring the solution directly into an acidified KI solution and titrating with standardized $Na_2S_2O_3$ with a starch indicator.

Ferricyanide was determined by measuring the absorbance at 420 mμ.

Ferrocyanide was determined by adding acidified $FeCl_2$ solution and measuring the absorbance of the colored complex at 200 mμ.

Bromine on resins was determined by soaking the resin in 10 percent NaOH, and distilling the supernatant in an acidified solution using the modified cyanide determination apparatus shown in Figure 1. The KI solution was titrated with $Na_2S_2O_3$ using starch indicator.

Bromide was determined by titrating potentiometrically with standard $AgNO_3$ solution.

Bromide resin weight was determined by air drying small amounts of resin on a buckner funnel - vacuum flash apparatus until all cohesion between resin beads was lost.

Rebromination of resins was accomplished by utilizing the apparatus shown in Figure 2 unless otherwise indicated. Bromine (ℓ) was added to 1.5 liters of distilled water in the vacuum flask and stirred to dissolve bromine into the water, which was pumped through a column filled with resin until the top beads attained a deep red color.

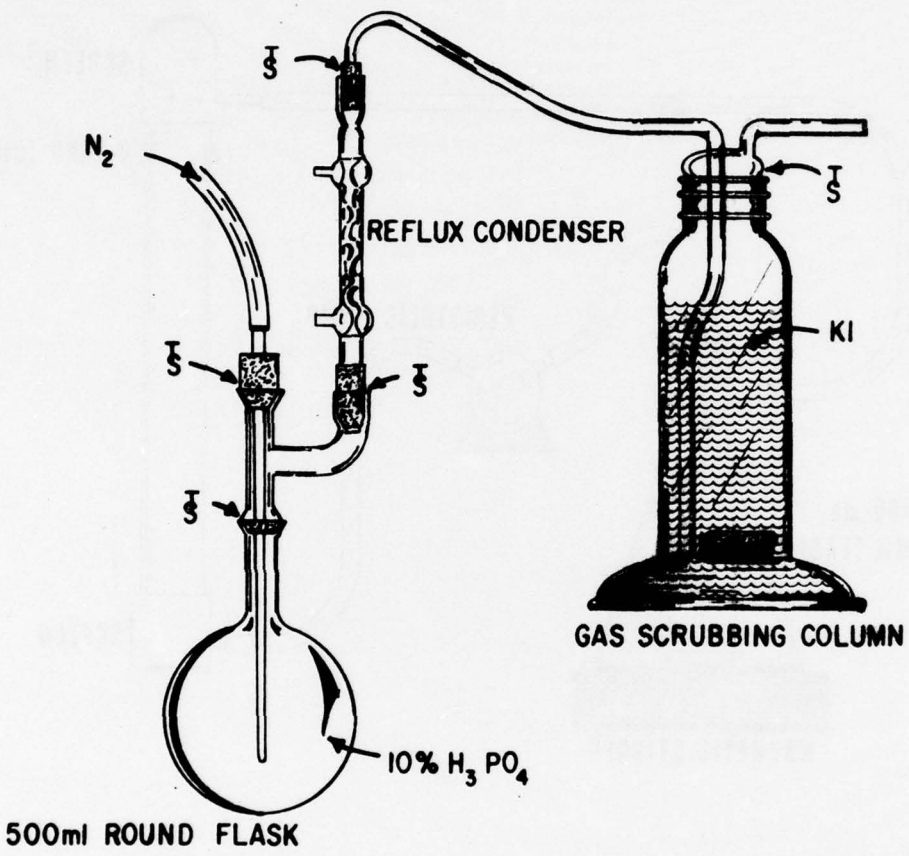

Figure 1. Modified Cyanide Apparatus for Determination of Bromine on Resin

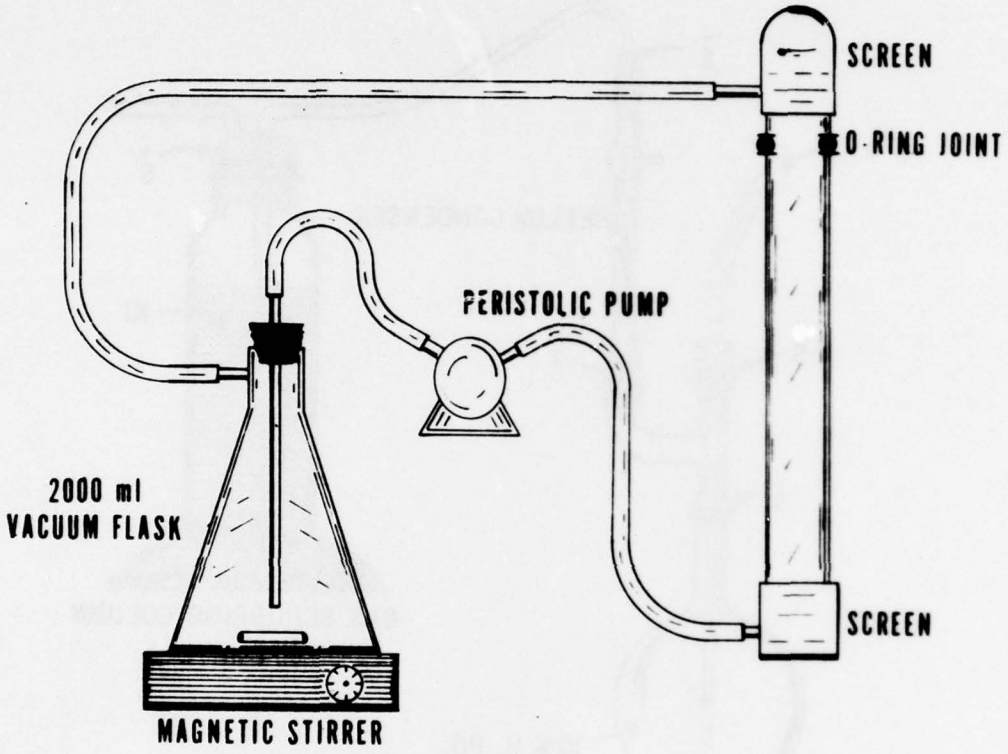

Figure 2. Bromination Apparatus

SECTION III

EXPERIMENTAL METHODS

The experimental methods employed in this study were designed to determine the mechanism by which bromine is liberated from the resin into solution, whether or not other resins can be brominated, to examine methods of regenerating actual waste ferricyanide bleach, and to determine the life-span of the resin under conditions of simulated use.

In order to determine the parameters controlling transfer of bromine from the resin, a series of tests were performed using a small (0.197 cm^2) column filled with 3 gm of resin to a height of 15 cm. Solutions consisting of distilled water, 500 mg ferrocyanide ion, and 500 mg ferrocyanide and ferricyanide ions were passed through the column at various flow rates. The purpose was to determine the effect of flow rate on the transfer rate of bromine into solution. Increasing the flow rate results in a decrease in the boundary layer thickness around each resin bead and a decrease in the bromine concentration surrounding each bead. If the diffusion of bromine from the resin bead into the boundary layer (D_1) is much slower than the diffusion of bromine from the boundary layer into the bulk solution (D_2), and if the reaction between the bromine and the ferrocyanide occurs in bulk solution, then increasing the flow rate will have no effect. If both diffusion rates were of the same order of magnitude, the flow rate would cause a faster transfer rate up to some flow rate, at which point no further increase in transfer rate would occur as D_1 would become limiting, and control the overall transfer rate. If D_1 is much greater than D_2, an increase in flow rate will cause an increase in the overall transfer rate. Bromine transfer rates were calculated by measuring the bromine in the distilled water and increasing the ferricyanide concentration for the other two solutions.

If the reaction between the bromine and ferrocyanide should occur on the resin, it would be expected that there be much less transfer of bromine into the distilled water than into the ferrocyanide solutions. Because the column used in these tests was so small, it was expected that boundary effects around the column wall would be significant. Therefore, the results of these tests should not be considered strictly quantitative.

In a preliminary report[2], the resin was observed to be subject to fouling. In order to assess the effect of this fouling on the transfer of bromine, two column studies were conducted. Fresh brominated resin was placed in a column and contacted with a 500 mg ferrocyanide solution for a short period of time. The next day the resin, which had become fouled overnight, was again contacted with the ferrocyanide solution.

---

[2] Ibid

Column tests were performed with solutions containing much larger amounts of ferrocyanide in order to approximate concentrations found in actual spent bleach. The bromine transfer rate was calculated from the ferrocyanide data assuming a stoichiometric reaction.

Batch tests were performed to determine if resins other than the commercial bromine resin could be brominated. Different resins were placed in a 125 ml conical flask with 75 ml of distilled water and 2 ml of bromine, which was slowly added while the resin was being stirred.

Other column tests were conducted on resins brominated in a column. Time versus bromine transfer rate graphs were prepared to compare the characteristics of these resins with the commercially prepared resin.

Batch tests were conducted to determine the operational characteristics of such a system. Two-liter batches of solution (either bleach or synthetic bleach) were placed in a 4-liter beaker and stirred with sufficient vigor to keep the resin in suspension. Ferrocyanide was determined at various times over a 4-hour period.

A series of bromination batch tests was conducted in the column apparatus on a single selected resin sample. After each bromination cycle, the resin was air-dried, weighed, defouled by refluxing with 10 percent H_3PO_4 solution, and was then returned to the column apparatus for the next cycle.

SECTION IV

RESULTS

Data from the first series of tests are presented in Figures 3, 4, and 5. In all three solutions, an increase in flow rate resulted in an increase in overall transfer rate to the maximum flow rate obtainable with the equipment employed. The increase of the bromine transfer rate into the distilled water was less than the solution containing ferrocyanide, due perhaps to the fact that the bromine was not instantaneously removed by reacting with the ferrocyanide, thus decreasing the driving force caused by the concentration gradient between the concentration in the boundary layer and that in the bulk solution. Because the curve for the distilled water is so similar to that of the solution containing ferrocyanide, it appears that the reaction occurs in the bulk solution.

Fouling was determined not to prevent bromine transfer from the resin. The results from day 2 using the same fouled resin from day 1 indicate that the fouling does affect the performance, as the transfer rate increased with time (see Figure 6 and 7). Note the low flow rates employed and the fact that only 50 mg of bromine was removed on the first day out of a total of 900 mg on the resin.

Further batch tests were conducted on the resin to study the fouling mechanism. The resin was rinsed thoroughly in distilled water following a column test, but still became fouled overnight. Other resin was contacted with a ferricyanide solution and a ferrocyanide solution and rinsed. This latter resin still became fouled. It appears that the fouling mechanism results from ferricyanide which has become absorbed into the resin, and that it is not feasible to prevent it from occurring by removing the resin promptly from the ferricyanide after use.

Data from tests with higher ferrocyanide are similar to that with lower concentrations, except that the transfer rates for a given flow rate are higher (see Figures 8, 9, and 10). The rate still falls off rapidly as a significant portion of the bromine is removed from the resin. After about half the bromine is removed, the rate falls off rapidly until the bromine is exhausted. Doubling the flow rate from 25.85 to 51.78 mg/min-cm^2 and decreasing the ferrocyanide concentration from 12 gm to 4.12 gm did not change the slope of the curve.

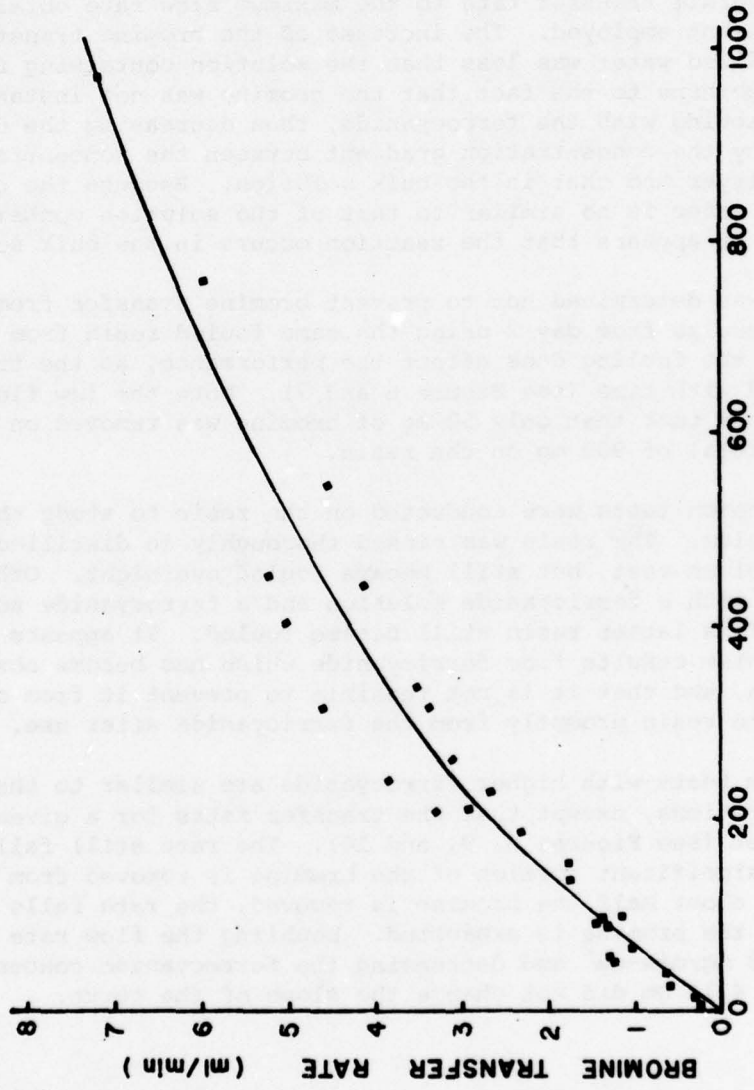

Figure 3. Bromine Transfer into Distilled Water (3 gm resin)

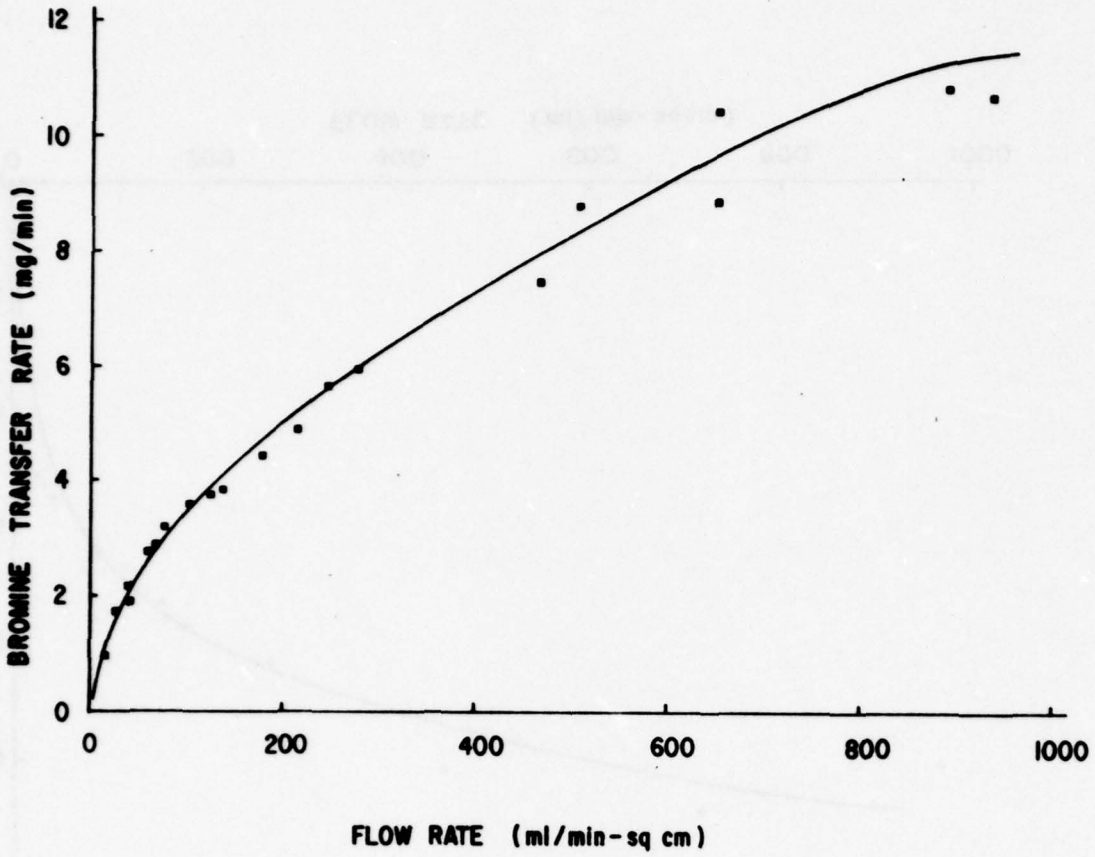

Figure 4. Bromine Transfer into 500 mg/l Fe $(CN)_6^{-4}$ Solution 3 gm resin

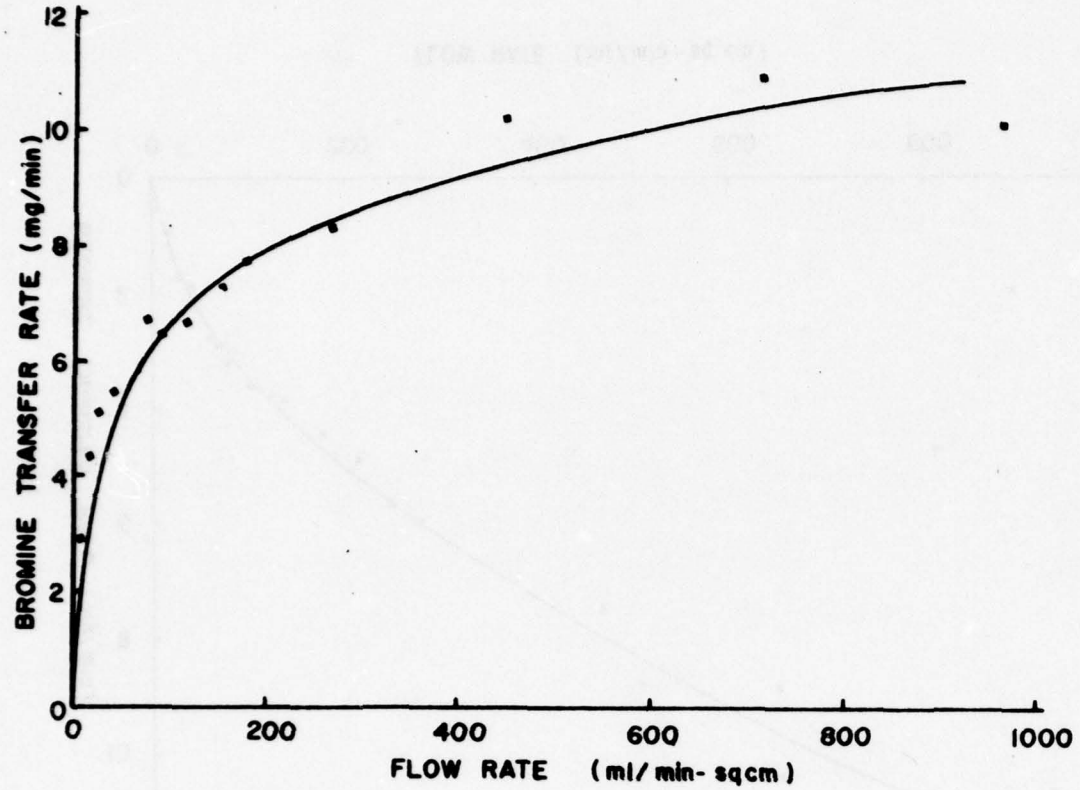

Figure 5. Bromine Transfer into 500 mg/l Fe $(CN)_6^{-4}$ and 500 mg/l Fe $(CN)_6^{-3}$ Solution (3 gm resin)

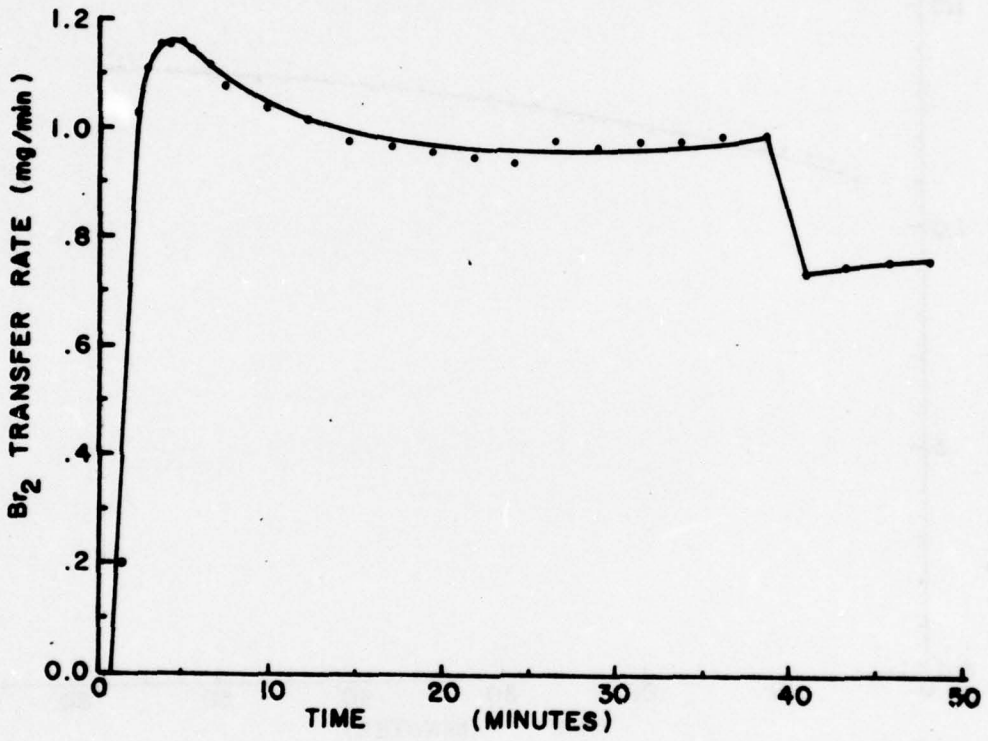

Figure 6. Br_2 Transfer for New Resin, Day 1 Flow Rate = 15.3 ml/min-cm^2
10^{-4} 500 mg/l Fe $(CN)_6$ Solution (3 gm resin)

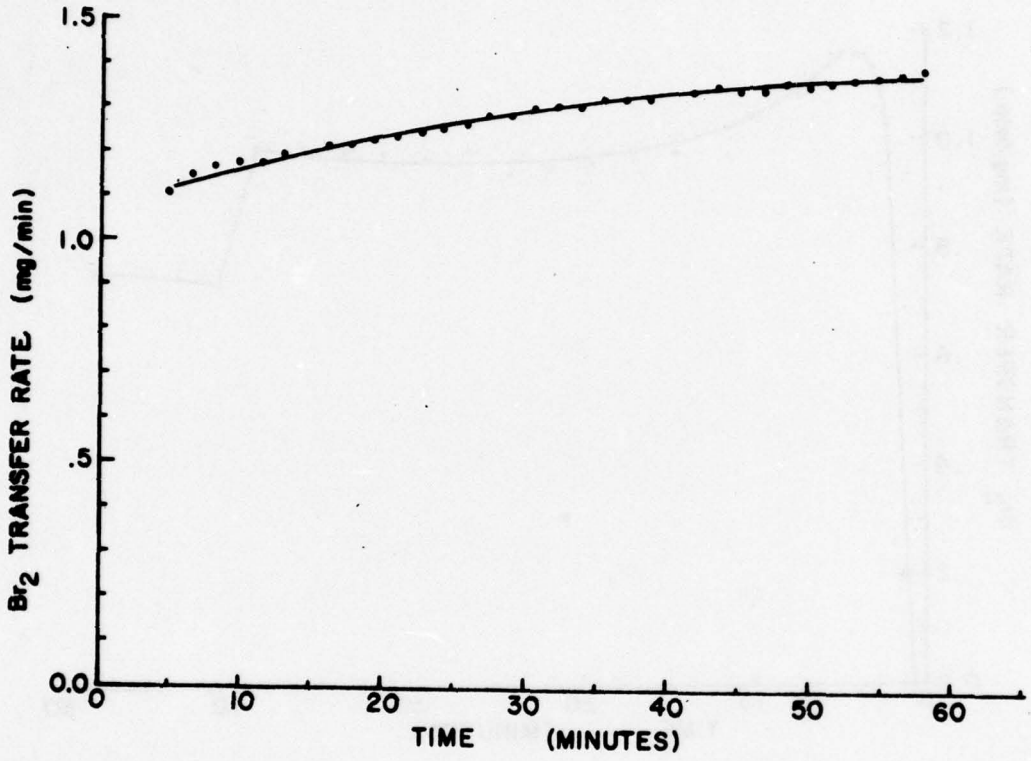

Figure 7. Br_2 Transfer for Fouled Resin, Day 2 Flow Rate = 22.8 ml/min-cm^2
500 mg/l Fe $(CN)_6^{-4}$ Solution (3 gm resin)

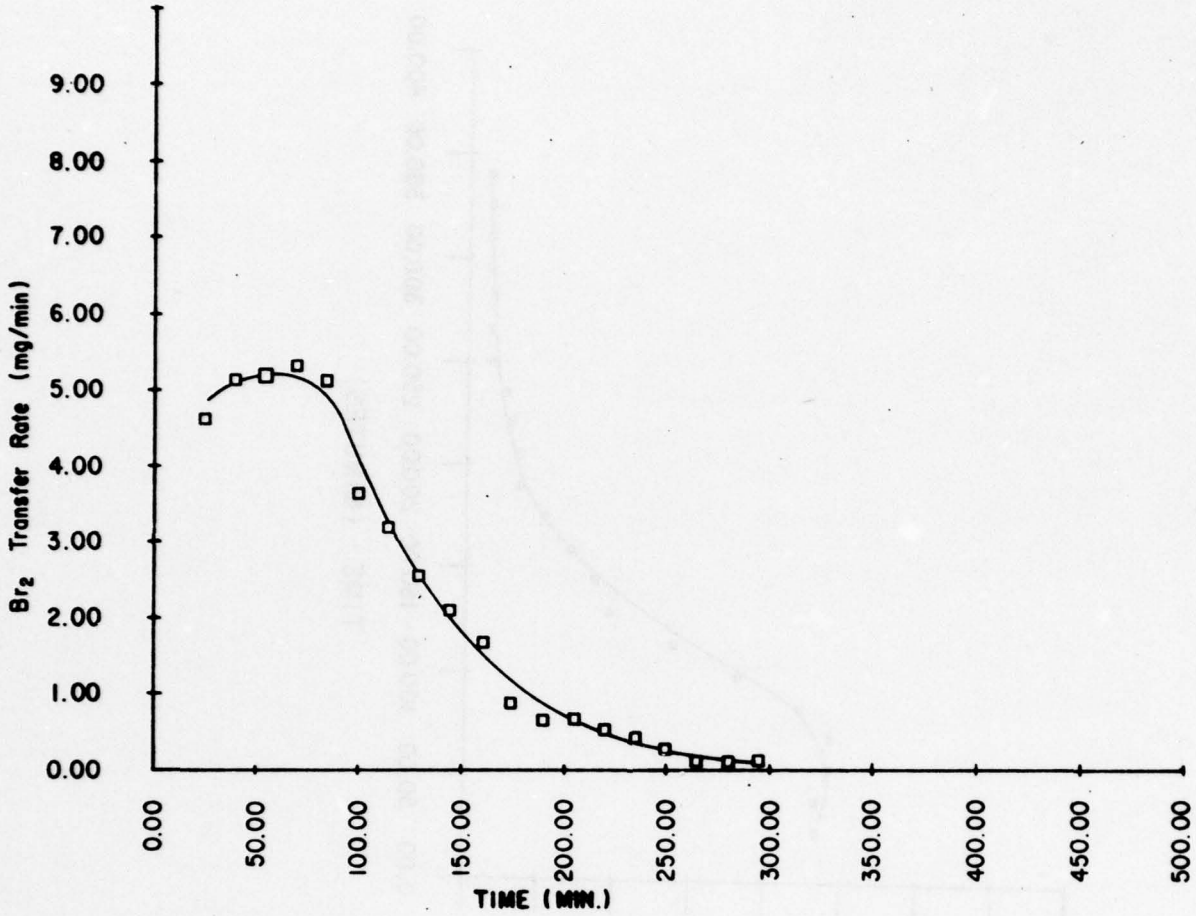

Figure 8. Column Test with 3 gm Bromine Resin 12 gm/l Fe $(CN)_6^{-4}$ Solution 25.85 ml/min-cm^2

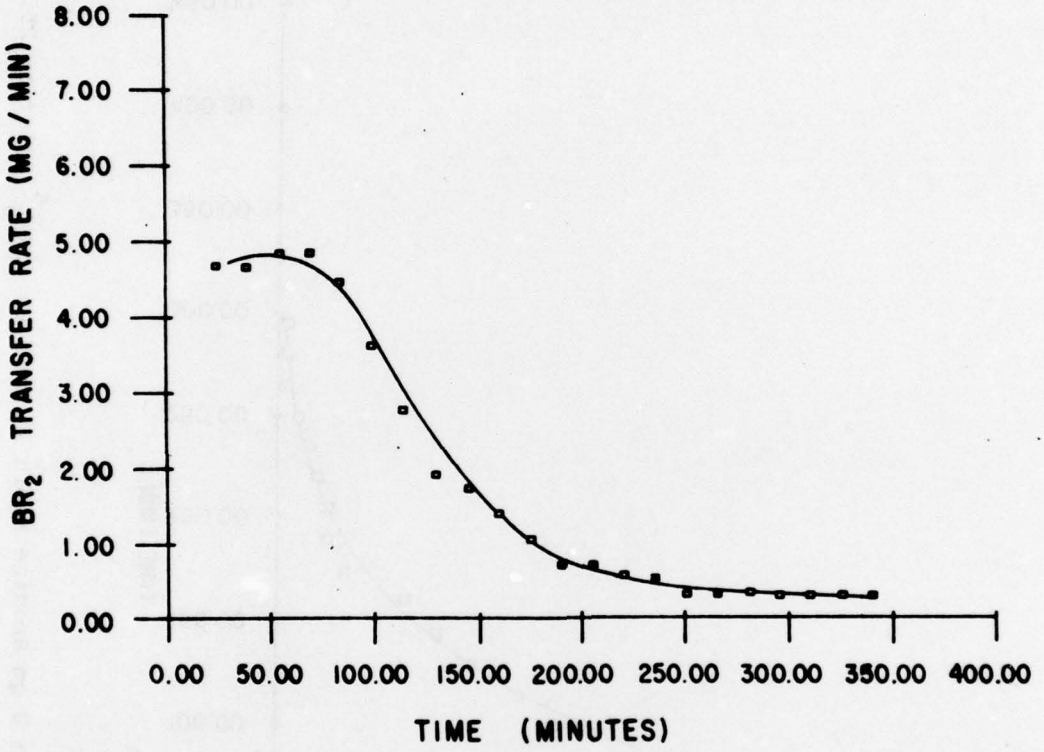

Figure 9. Column Test with 3 gm Bromide Resin 4.12 gm/l $Fe(CN)_6^{-4}$ Solution 51.78 ml/min-cm^2

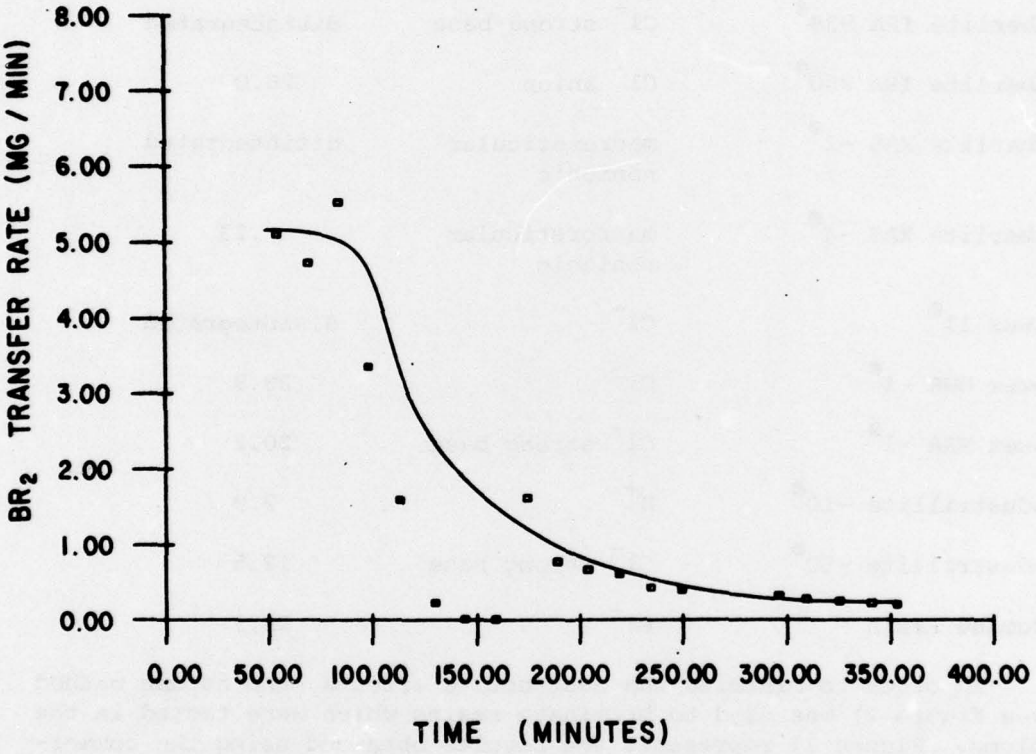

Figure 10. Column Test with $\frac{3}{4}$gm Bromide Resin
12 gm/l $Fe(CN)_6^{-4}$ Solution
51.78 ml/min-cm^2

Resins other than the Dowex 21-K®, commercially prepared, can be brominated (see Table 1). It appears that the anionic form of the resin does not have to be Br^- in order to brominate the resin. However, a $ClBr_x^-$ form may be present, as the cationic resins would absorb only a small amount of bromine.

TABLE 1. BROMINATED RESIN RESULTS

Resin	Form	Br_2 Capacity obtained %
Amberlite IR 120®	H^+ strong acid	0.7
Amberlite IRA 938®	Cl^- strong base	disintegrated
Amberlite IRA 900®	Cl^- anion	26.0
Amberlite XAS -2®	macroreticular nonionic	disintegrated
Amberlite XAS -4®	macroreticular nonionic	.23
Dowex 11®	Cl^-	disintegrated
Dowex MWA -1®	Cl^-	28.9
Dowex MSA -1®	Cl^- strong base	20.2
Industrillite -10®	H^+	2.9
Industrillite -50®	Cl^- strong base	12.5
Bromine Resin	Br^-	28.1

In order to minimize the destructive effects, the column method (see Figure 2) was used to brominate resins which were tested in the column. Figure 11 represents the results obtained using the commercially prepared resin. Other resins were very similar (Figures 12, 13, and 14); the bromine transfer rate declining as the bromine on the resin became exhausted. This would suggest that the Dowex 11® resin in particular can be substituted for the Dowex 21-K® with nearly identifical results.

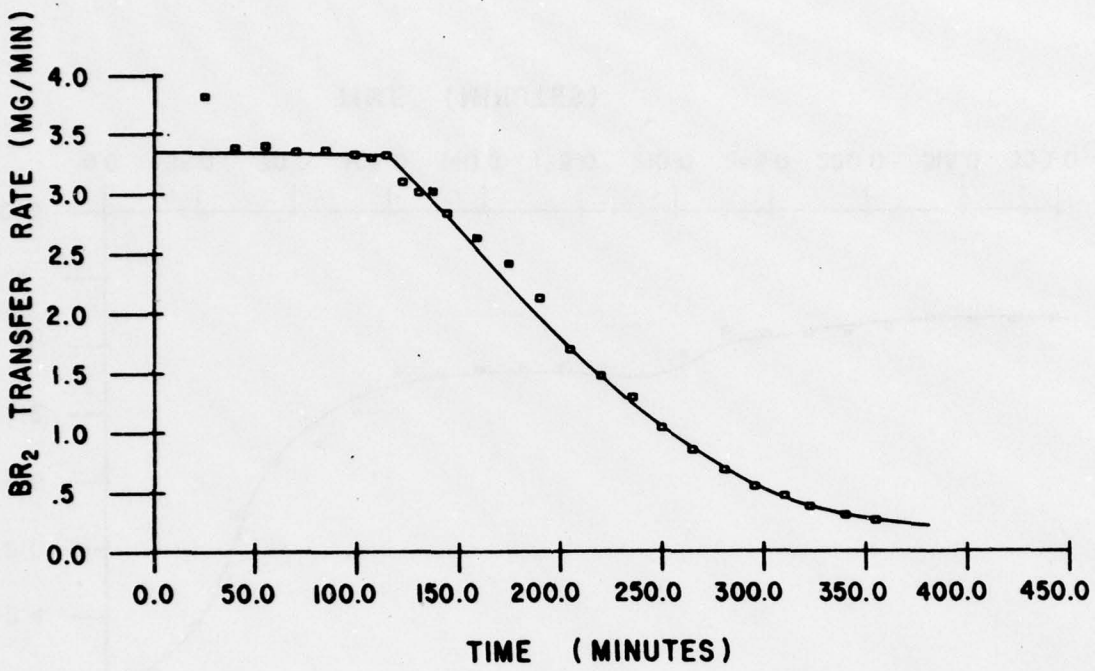

Figure 11. Column Test with 3 gm Bromine Resin 750 mg/l Fe $(CN)_6^{-4}$ Solution 65.2 ml/min-cm^2

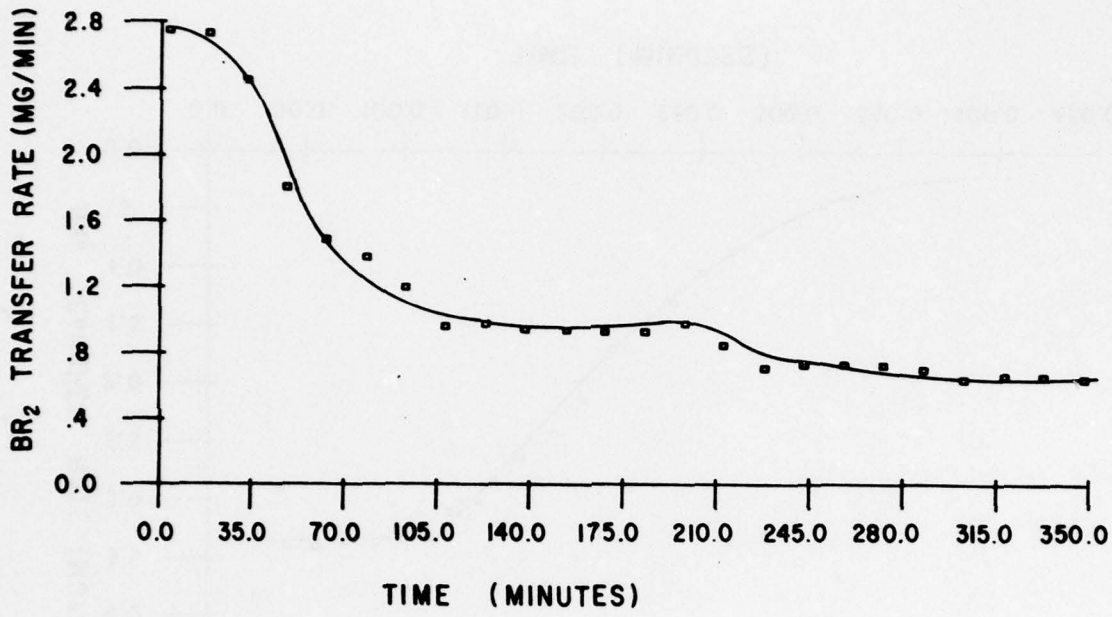

Figure 12. Column Test with 3 gm MSA-1 Resin 750 mg/l Fe $(CN)_6^{-4}$ Solution 63.60 ml/min-cm^2

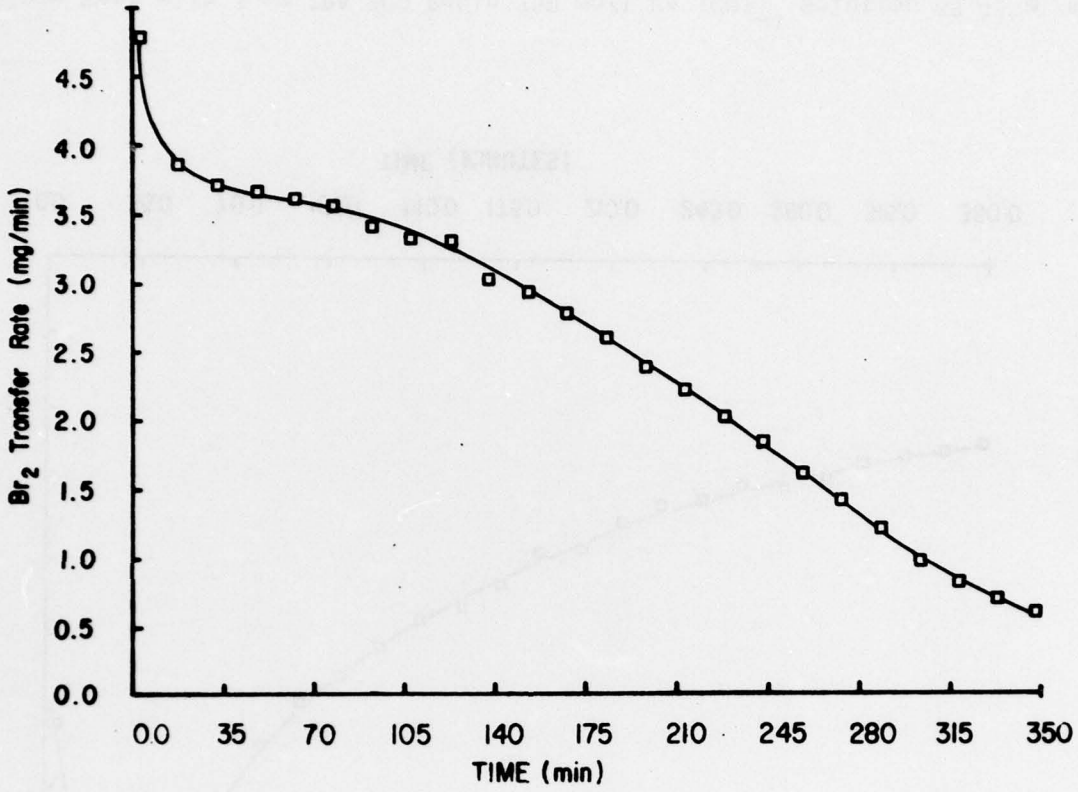

Figure 13. Column Test with 3 gm Dowex-11 Resin 750 mg/l FE $(CN)_6^{-4}$ Solution 62.44 ml/min-cm^2

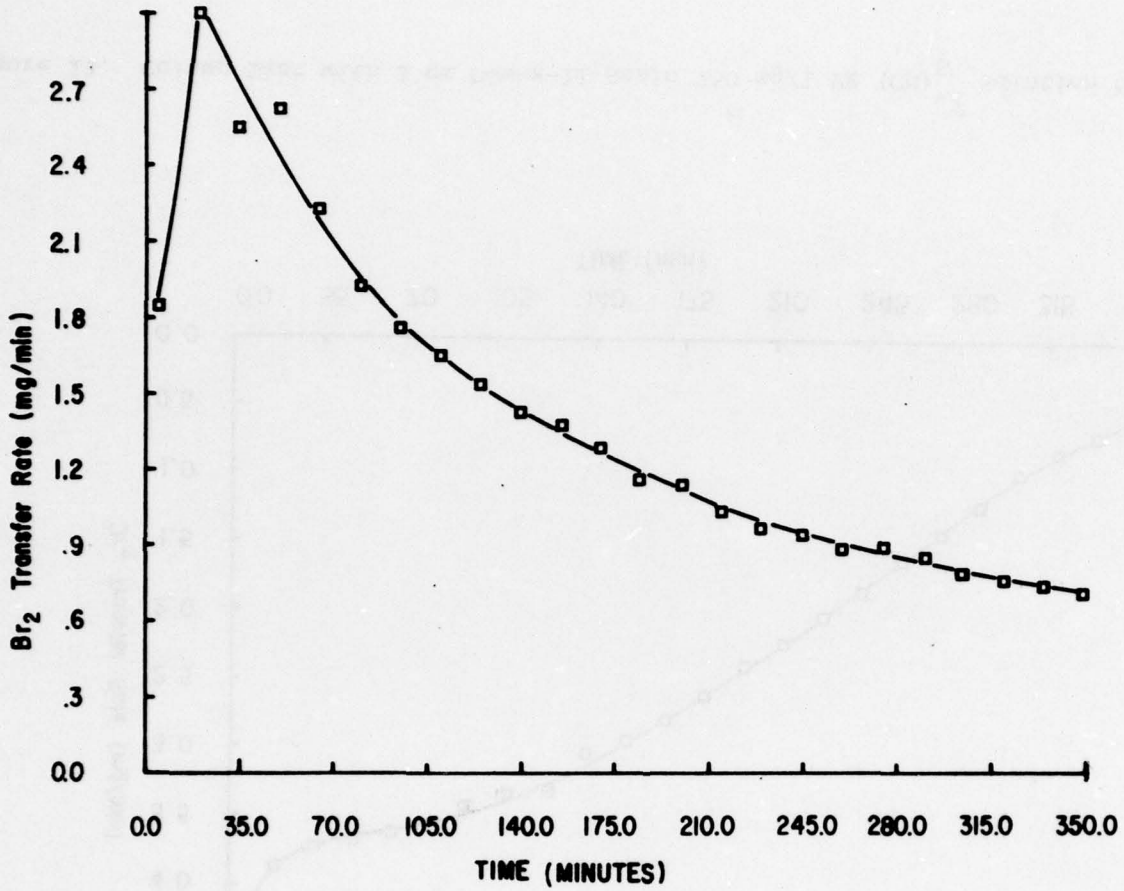

Figure 14. Column Test with 3 gm IRA 900 Resin 750 mg/l Fe $(CN)_6^{-4}$ Solution 63.45 ml/min-cm^2

Batch tests indicate that such a system is feasible provided that sufficient contact time is allowed (see Figure 15). The batch test using 45 gm of resin utilized 11.5 gm of the 13.5 gm of bromine available. A reduction of the ferrocyanide to the level obtained in this test would be sufficient to allow its reuse, provided sufficient concentration is obtained.

The lifespan of the resin is slightly more than 4 cycles (see Figure 16), as determined by summing the weights at the end of each cycle and dividing by the original weight of the resin (30 gm). Using the cost figures in the preliminary report, this increases the variable cost of 9 liters of regenerated bleach from 0.81 to 1.20 dollars, compared to 4.95 dollars for 9 liters of new bleach.

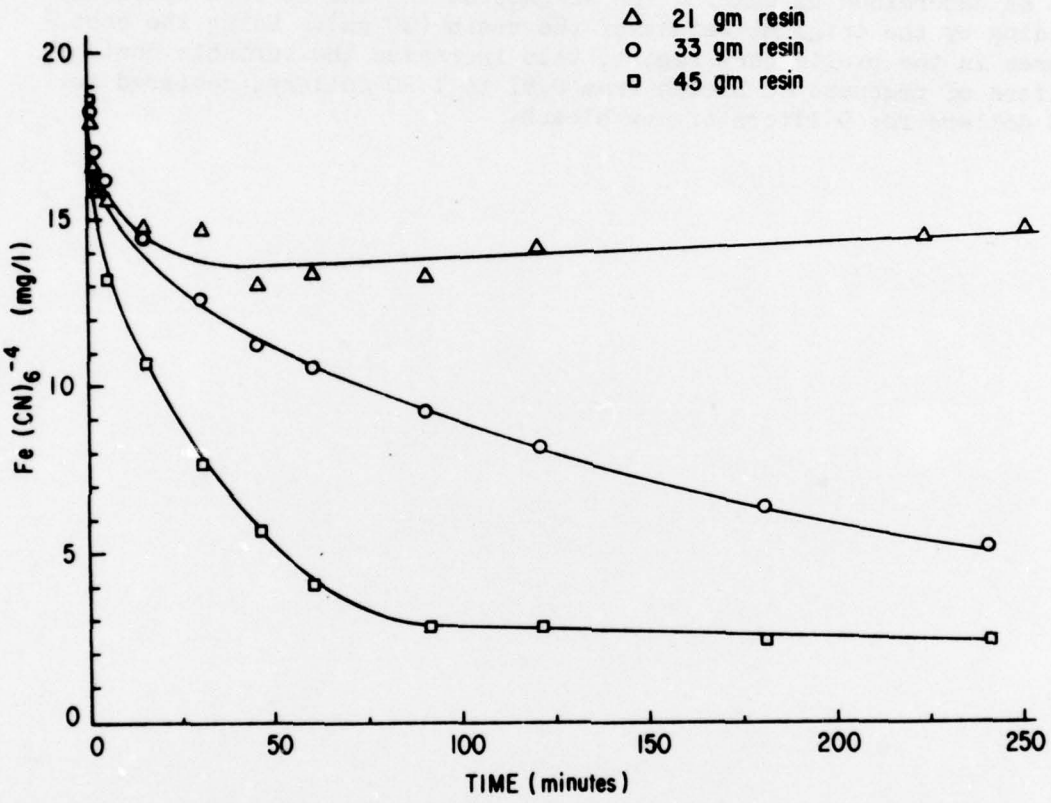

Figure 15. Batch Tests

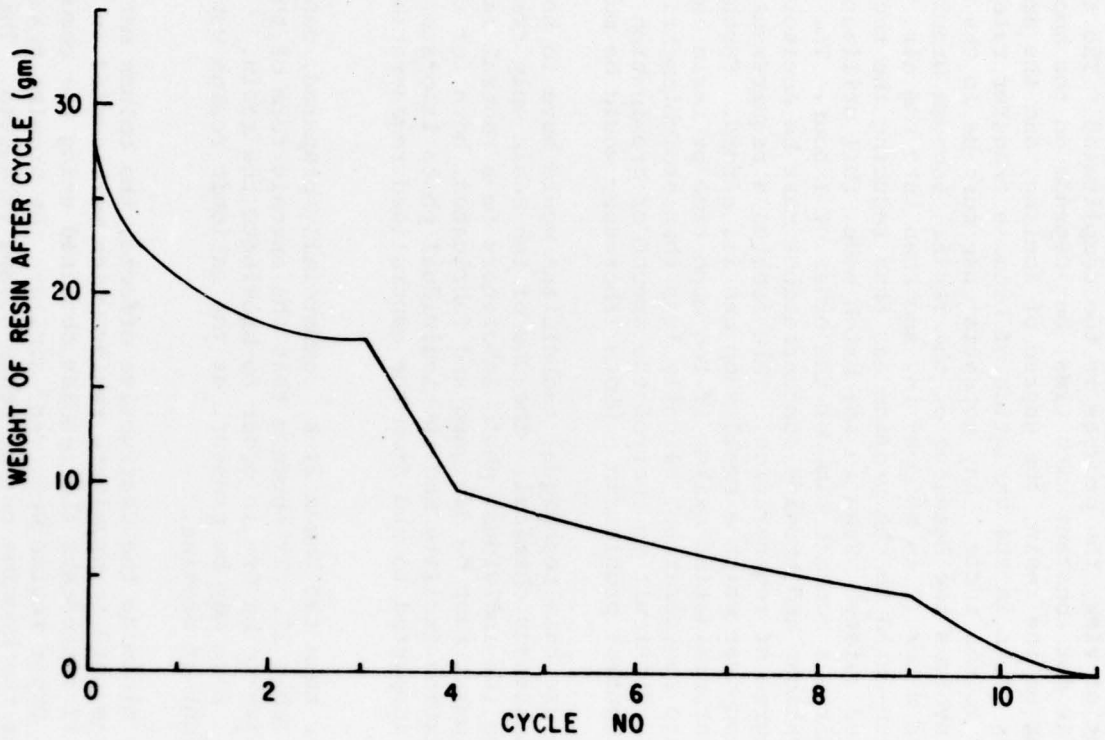

Figure 16. Resin Deterioration with use Cycle: Bleach Regeneration, Defouling, Resin Regeneration

SECTION V

CONCLUSIONS

The use of this technique to regenerate spent ferricyanide bleaches in small photoprocessing shops is unfeasible for several reasons. From a technical point of view, the process is too complicated. The transfer rate of bromine is not constant with time, but depends on the amount of bromine remaining on the resin, the degree of fouling, and the amount of turbulence, as shown in the variation of bromine transfer rate with flow rate in the column tests. Any potential use must be in the batch mode, but this involves the handling of the resin. Because bromine diffuses into the water it is shipped in, and then into the air, the resins will be subjected to the bromine gas thus reducing the technique's major advantage of safety. Even in the batch mode, full utilization of the bromine requires a contact time of the order of 1 hour. The ferrocyanide concentrations and bromide concentrations must be monitored to determine the degree of regeneration. This creates a requirement for space, equipment, and manpower which a small shop can ill afford. Furthermore, the danger of overbromination exists if too much time or resin is allowed. Even in presulfate regeneration, slightly less than stoichiometric amounts are used. It was difficult to control the amount of bromination in the laboratory; the control problem in a photo laboratory would be much greater.

In order to use this technique, technicians would have to be trained to work with a dangerous chemical. The use of the resin only transfers this problem from the individual photo laboratory to a central facility. Specialized equipment must be designed and fabricated, both for the centralized regeneration facility and the individual photo laboratory. Resin must be transported to and from the centralized regeneration facility.

Resins other than the Dowex 21-K, commercially prepared, can be brominated (see Table 1). It appears that the anionic form of the resin does not have to be Br^- in order to brominate the resin. However, a $ClBr_x^-$ form may be present, as the cationic resins would sorb only a small amount of bromine.

In order to minimize the destructive effects, the column method (see Figure 2) was used to brominate resins which were tested in the column. Figure 11 represents the results obtained using the commercially prepared resin. Other resins were very similar; the bromine transfer rate declining as the bromine on the resin became exhausted. This would suggest that the Dowex 11 resin in particular can be substituted for the Dowex 21-K with nearly identical results.

Although the process is feasible in the batch mode, the system which would be required involves too many steps, and requires too strict quality control to be practical for use in small photo laboratories.

Batch tests indicate that such a system is feasible provided sufficient contact time is allowed (see Figure 15). The batch test using 45 gm of resin utilized 11.5 gm of the 13.5 gm of bromine available. A reduction of the ferrocyanide to the level obtained in this test would be sufficient to allow its reuse, provided sufficient concentration is obtained.

The lifespan of the resin is slightly more than 4 cycles, as determined by summing the weights at the end of each cycle and dividing by the original weight of the resin (30 gm). Using the figures in the preliminary report, this increases the variable cost of 9 liters of regenerated bleach from 0.81 to 1.20 dollars, compared to 4.95 dollars for 9 liters of new bleach.

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